S&A FY03 ANNUAL REVIEW MEETING

In-Situ Real Time Measurements of Melt Constituents

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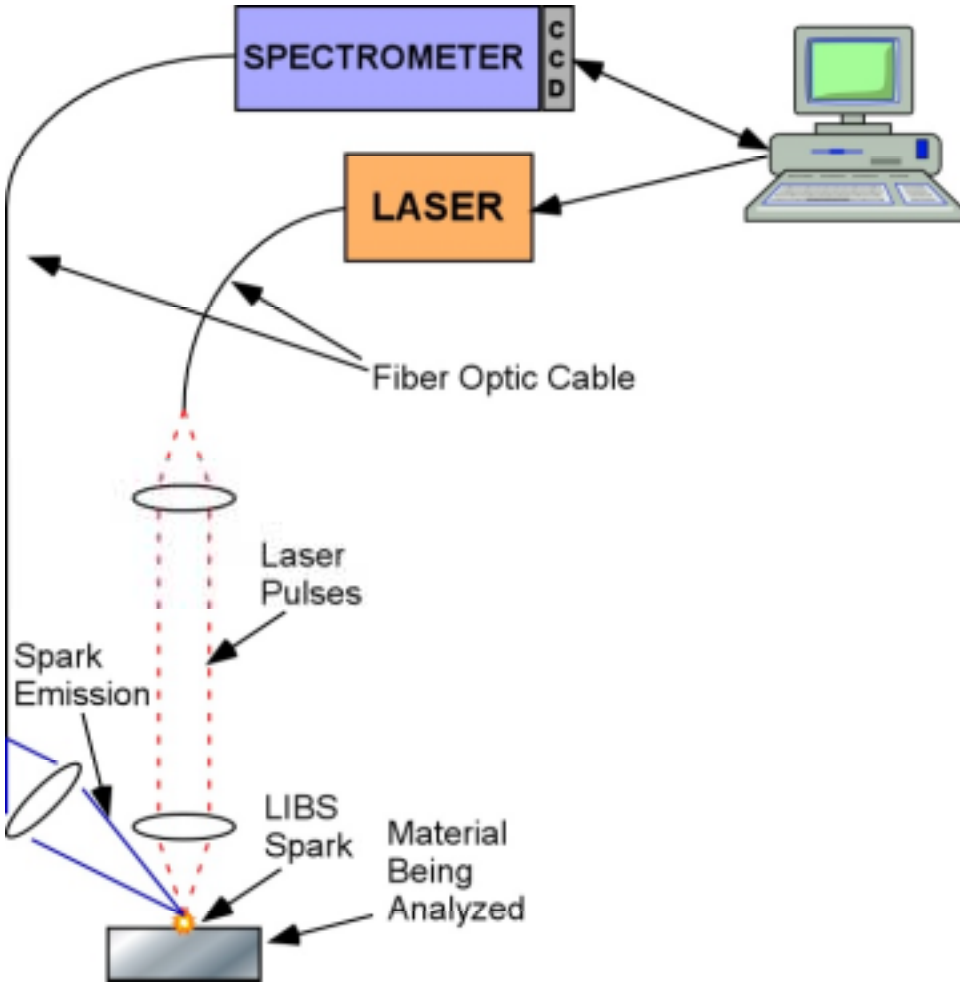
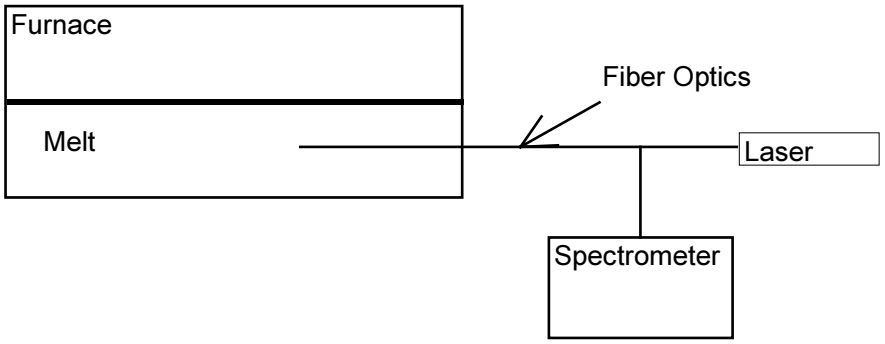
Project Overview

- **Project description**
  - Measure the Elemental Concentrations of Aluminum Melts During Processing, In Real-Time
- **Objectives**
  - Year 1: Develop laboratory scale LIBS probe for molten aluminum
  - Year 2: Develop pilot LIBS probe for molten aluminum
  - Year 3: Demonstration and Testing at Aluminum Plant
- **Overall goal**
  - Achieve Industry Accepted Accuracies, with Minimal Operator Training, and Minimal Maintenance

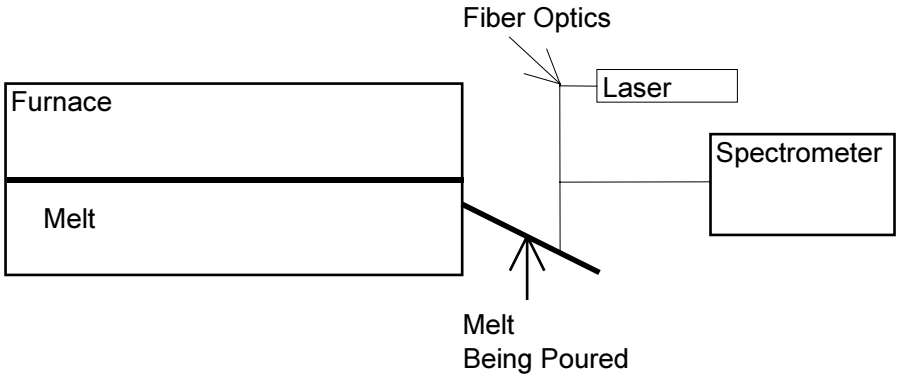
Laser Induced Breakdown Spectroscopy



Project Description



A. Measurements Made Within Furnace



B. Measurements Made During Pour

Technical Merit

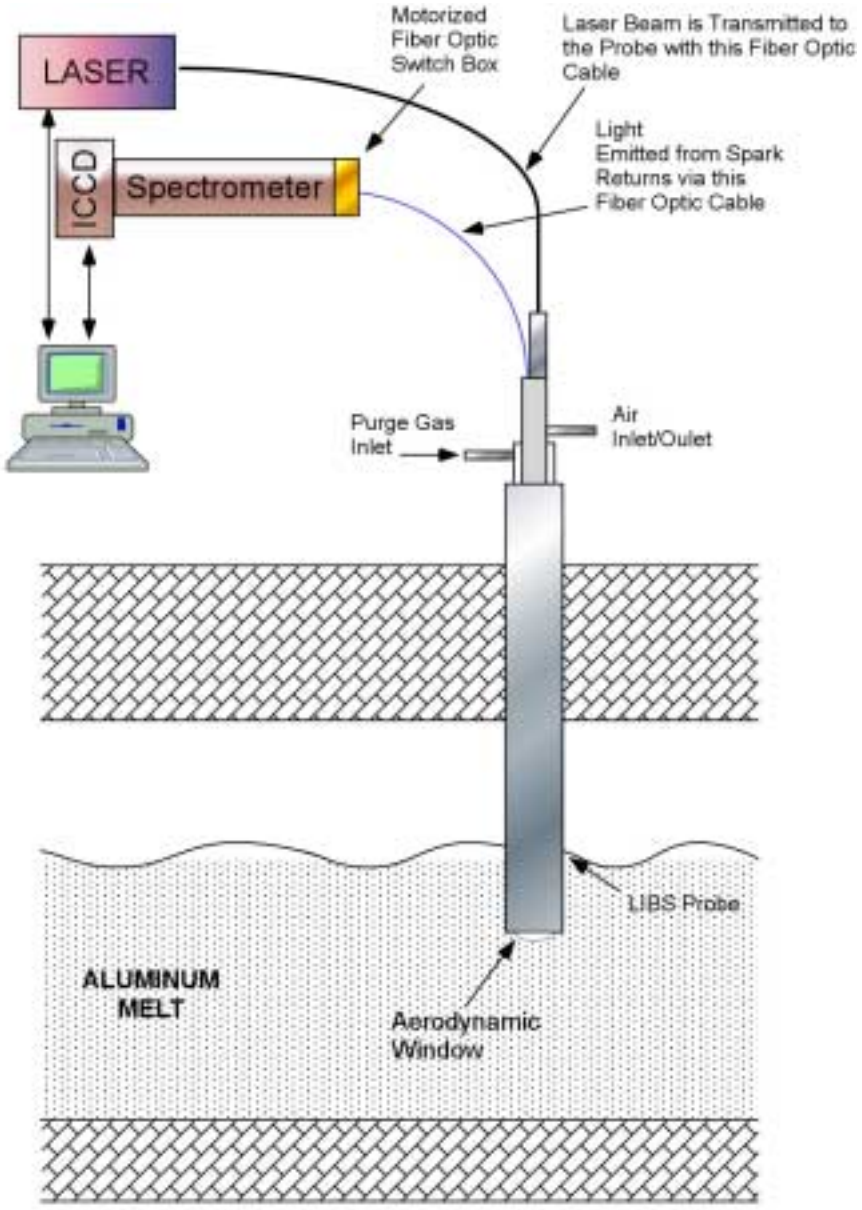
- **IOF's Can Use This Technology**
  - Aluminum – Molten
  - Aluminum – Alloy Separation
  - Glass - Molten
  - Glass – Batch and Cullet Sortation
  - Steel – Molten
  - Steel – Alloy Separation

Technical Merit

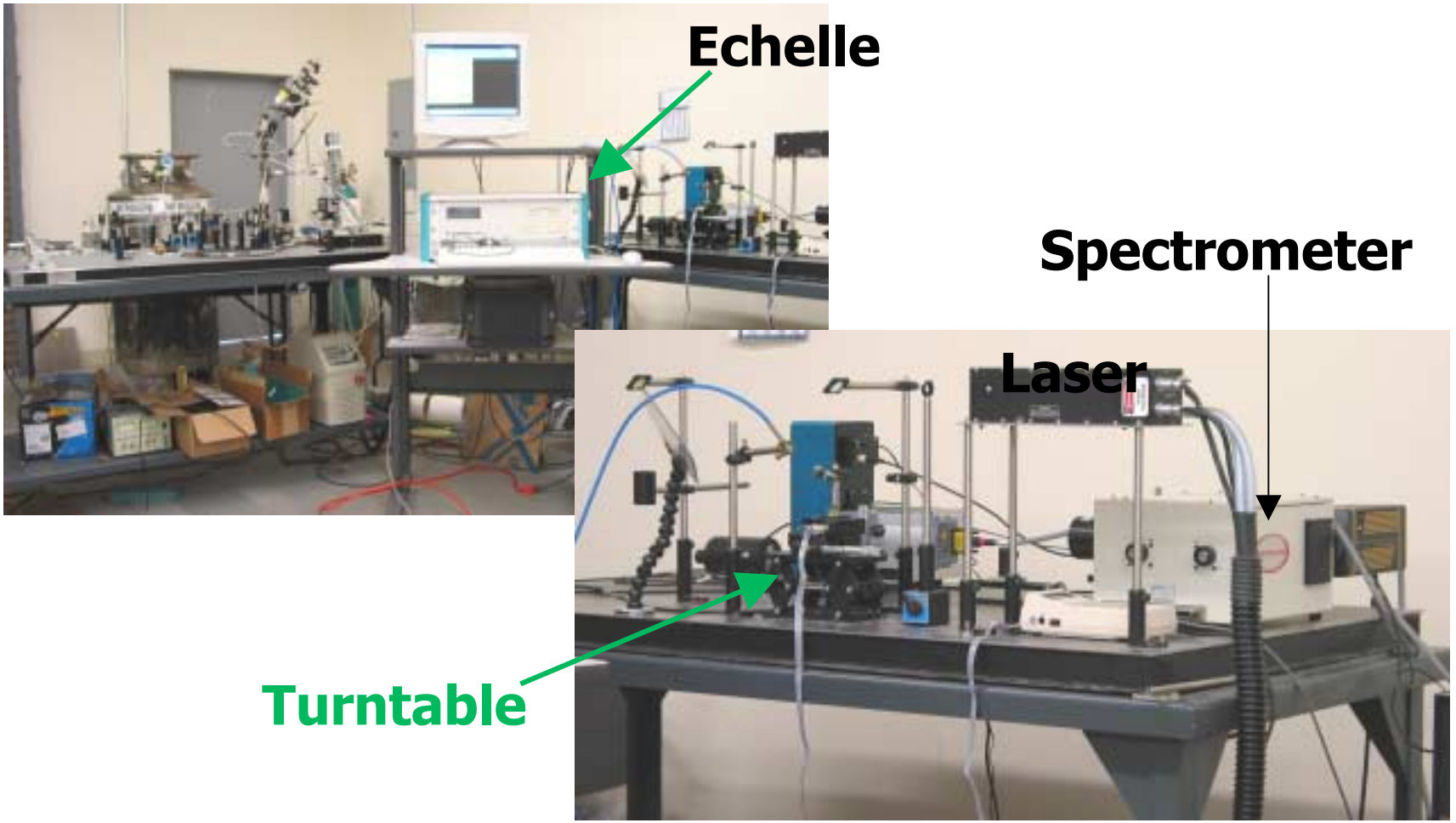
- **Contributes new information or technology to the S/C community**
  - Minimize Fluxing Agents Such as Cl and Fl compounds
  - Tighter Chemistry Tolerances
  - Reduces Processing Time
  - Energy Savings
  - Production Increase
  - Reduction in Waste Material
  - New Furnace Designs
  - Continuous Data will Allow Change from Batch to Continuous Furnace
  - This Information has Never Been Available to Industry Before.

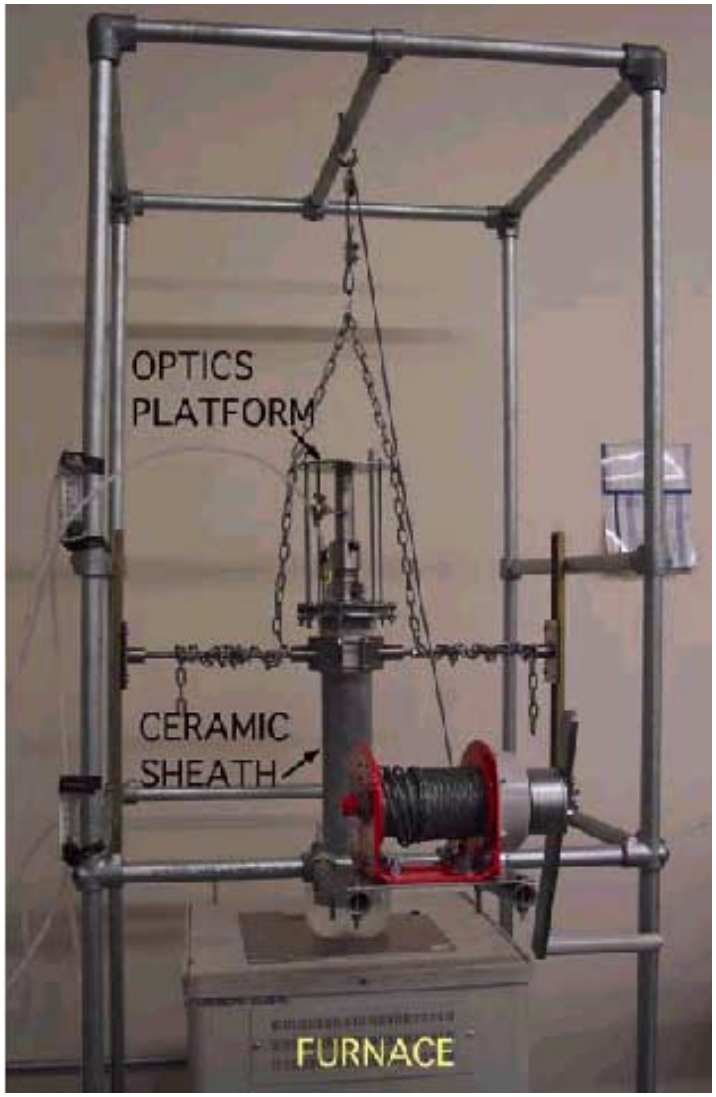
Accomplishments

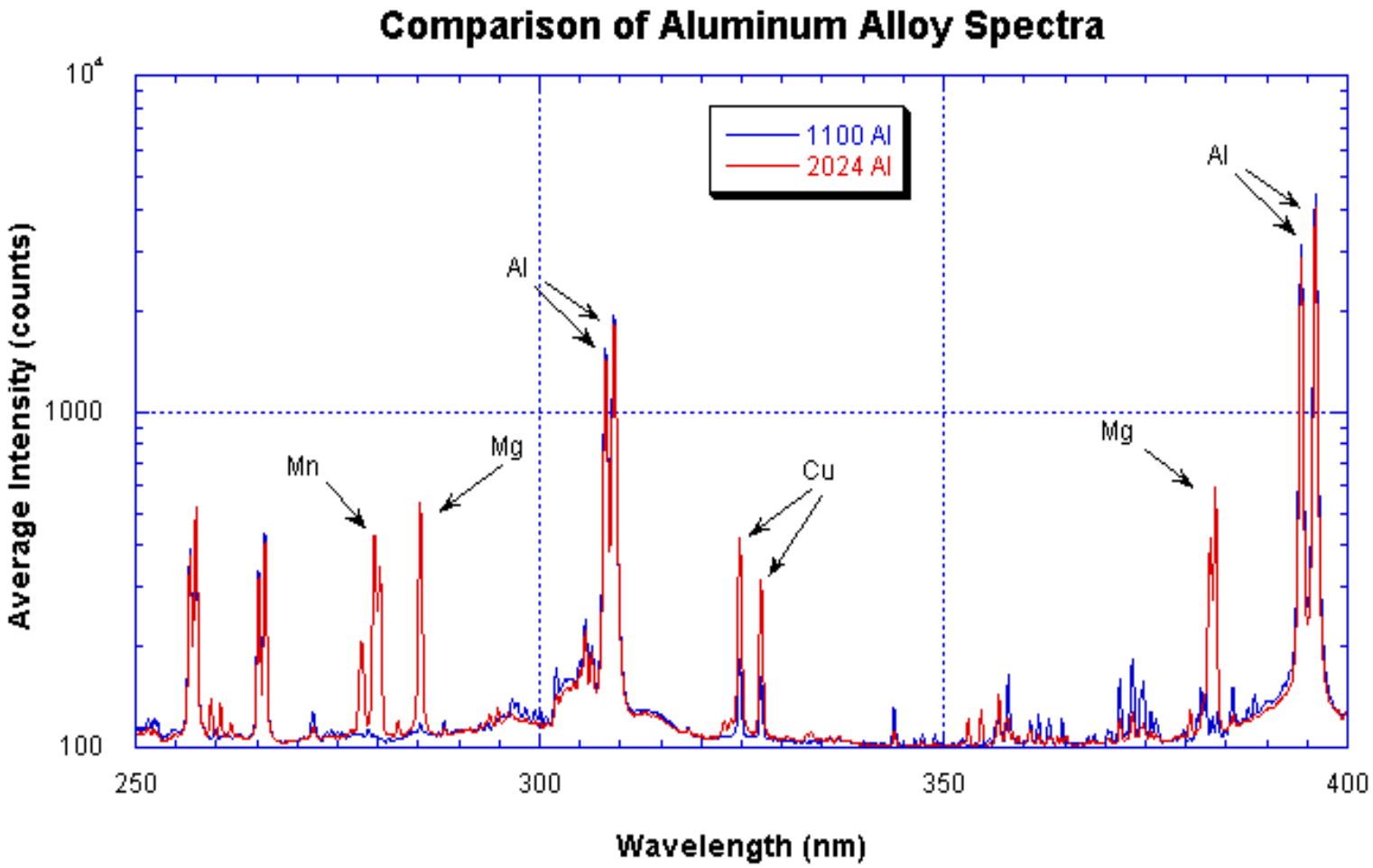
- **LIBS Probe Developed for *In-situ* Analyses of Molten Aluminum and Other Materials**
- **Melt Composition Accurately Measured at Any Point in the Melt**
- **For Aluminum, Commercialization Plan Completed**
- **Licensing Agreement Signed for Overseas and US Market**
- **Patent Application Filed in US, EU, Canada. Japan Pending.**
- **Desired Accuracy and Repeatability Achieved Using Calibration Free Techniques.**
- **User-Friendly Operating Software Completed**
- **Eye-Safe Certified**
- **Demonstration At Commonwealth Aluminum Prepared and Will Start End of June.**
- **First Overseas Sale Made**

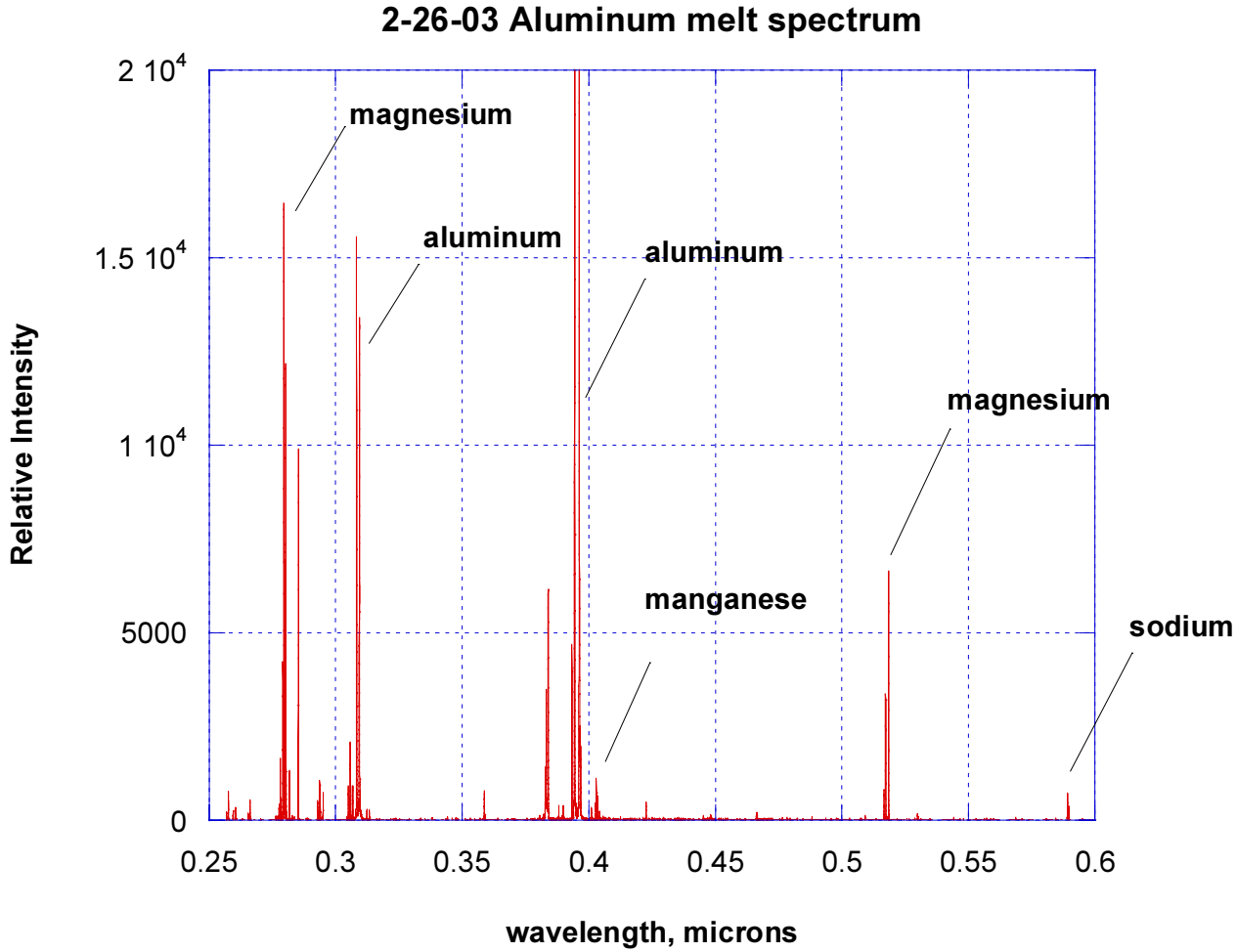

LASER
Motorized
Fiber Optic
Switch Box
Laser Beam is Transmitted to
the Probe with this Fiber Optic
Cable
ICCD
Spectrometer
Light
Emitted from Spark
Returns via this
Fiber Optic Cable
Purge Gas
Inlet
Air
Inlet/Oulet
LIBS Probe
ALUMINUM
MELT
Aerodynamic
Window

ERCo LIBS Facility

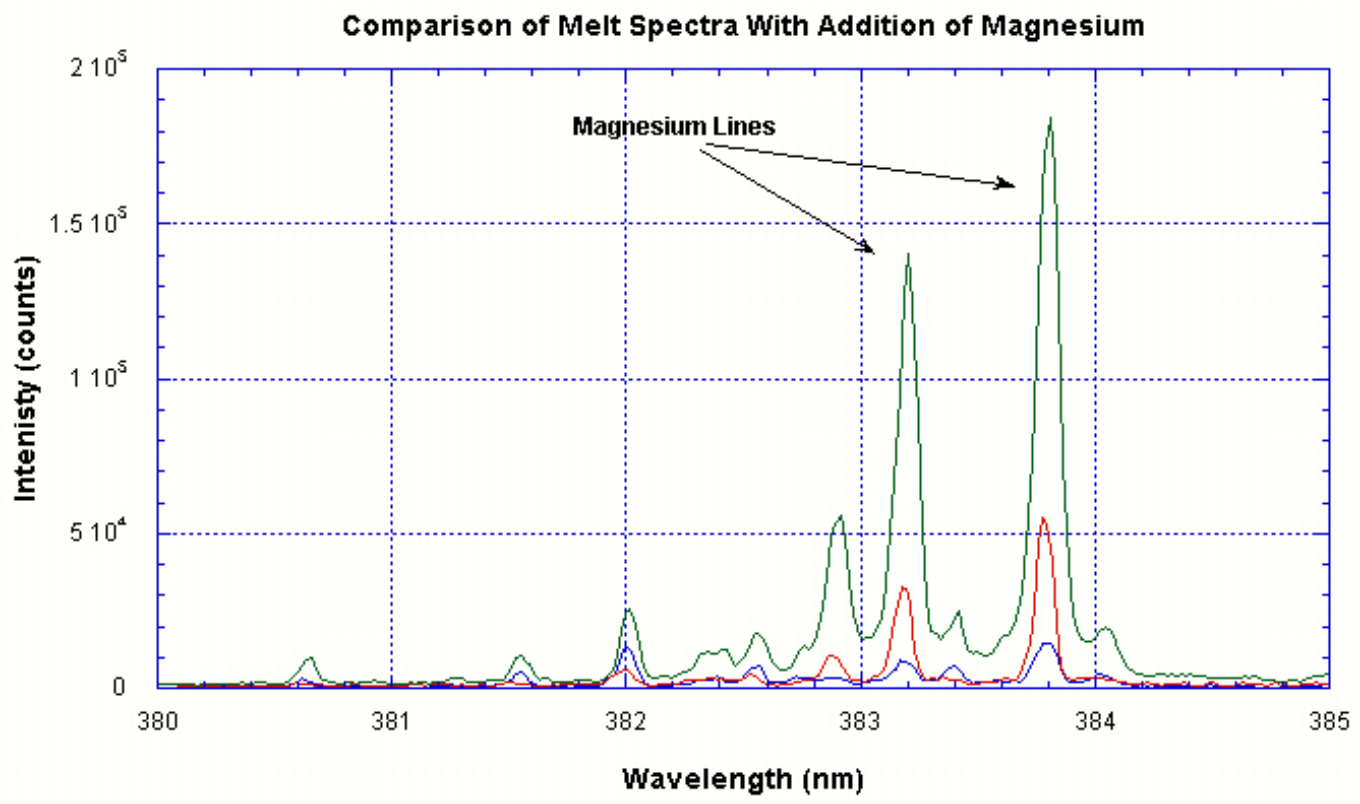


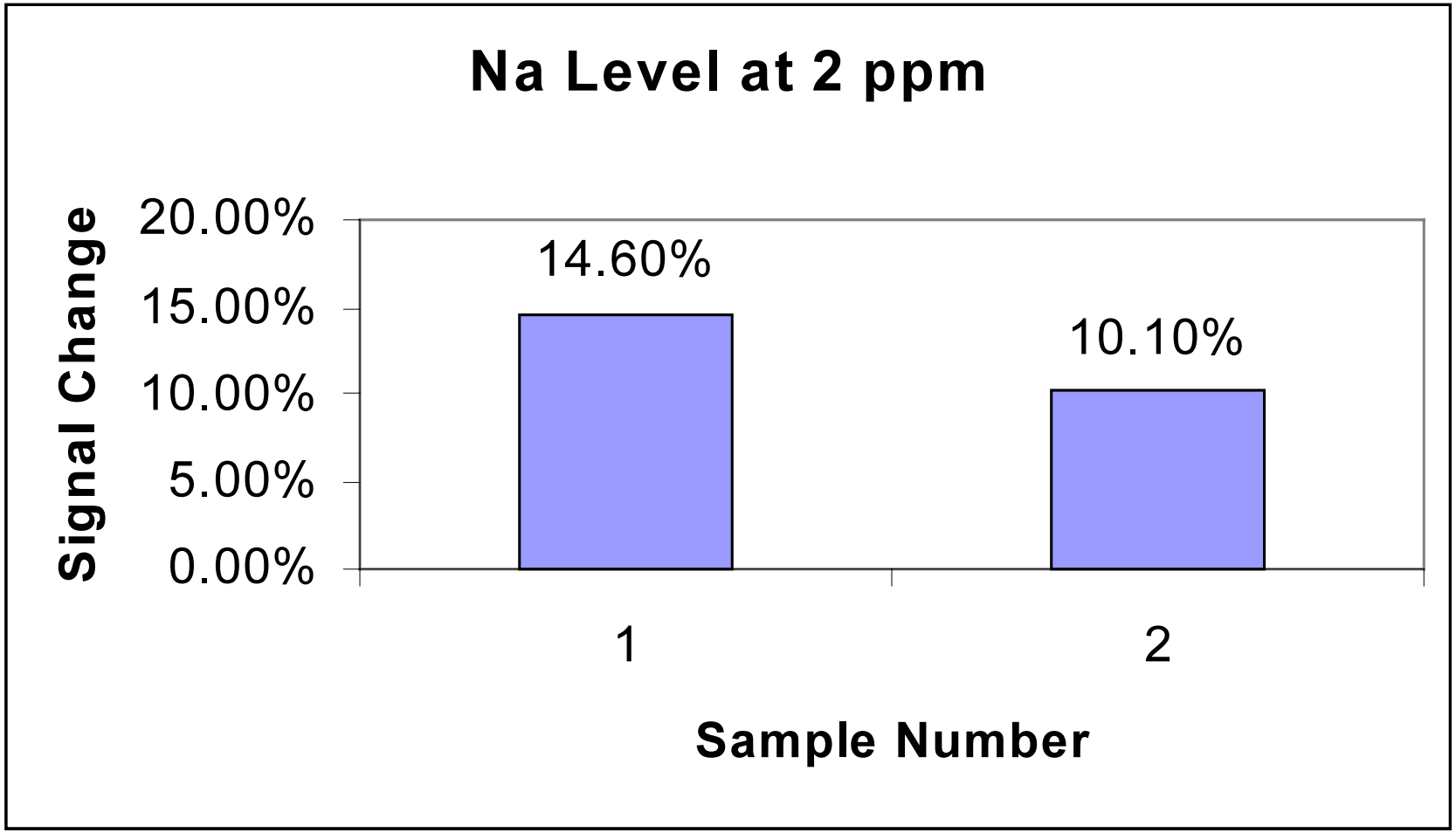

OPTICS
PLATFORM
CERAMIC
SHEATH
FURNACE


Comparison of Aluminum Alloy Spectra
10^4
1000
100
Average Intensity (counts)
1100 Al
2024 Al
Al
Mn
Mg
Cu
Mg
Al
250
300
350
400
Wavelength (nm)


2-26-03 Aluminum melt spectrum
2 10^4
1.5 10^4
1 10^4
5000
0
Relative Intensity
magnesium
aluminum
aluminum
magnesium
manganese
sodium
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
wavelength, microns

Mixing Measurements




Na Level at 2 ppm
Signal Change
20.00%
15.00%
10.00%
5.00%
0.00%
14.60%
10.10%
1
2
Sample Number

Results from Multivariate Calibration

	Reported Range - 5 Samples	Average Measurement Error
Na	**0-96 ppm**	**14.71%**
Al	**99.8%**	**0.0086%**
Si	**0.04%-0.06%**	**7.31%**
Fe	**0.06%-0.1%**	**5.35%**

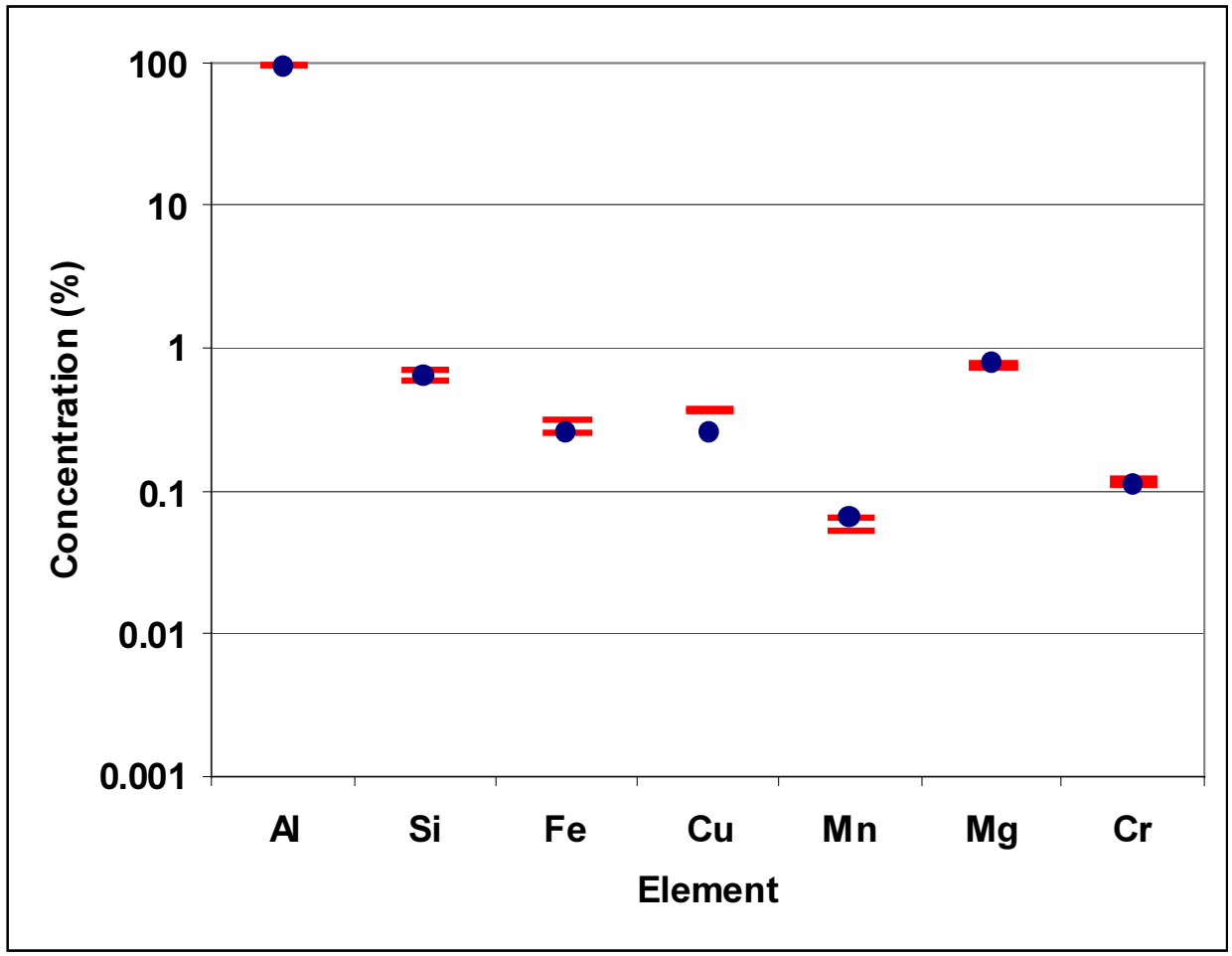
Calibration Free Method

- **Using Calibration Curves Will Require Molten Calibration Standards Due to Matrix Effects**
- **These Will need to be Replaced After Each Use.**
- **Difficult to Conduct in Plant Environment**

Calibration Free Method Models the Plasma

$$\overline{I_{\lambda}^{ki}} = FC_S A_{ki} \frac{g_k e^{-\left(E_k / k_B T\right)}}{U_S\left(T\right)}$$

Aluminum Measurements



Hardner Data

	Nominal	Measured	Error
Al	**80.5%**	**79.0%**	**1.8%**
Mn	**19.3%**	**20.6%**	**6.9%**

3003 Alloy
Average of 5 Data Sets

	Mn	Cu	Al
Reported	**1.28%**	**0.18%**	**98.54%**
LIBS Meas.	**1.33%**	**0.165%**	**98.51%**
Error	**3.9%**	**9.7%**	**0.03%**

3105 Alloy
Average of 5 Data Sets

	Mn	Mg	Si	Al
Reported	**0.52%**	**0.57%**	**0.02%**	**98.89%**
LIBS Meas.	**0.508%**	**0.568%**	**0.02%**	**98.92%**
Error	**2.3%**	**0.35%**	**0.0%**	**0.03%**

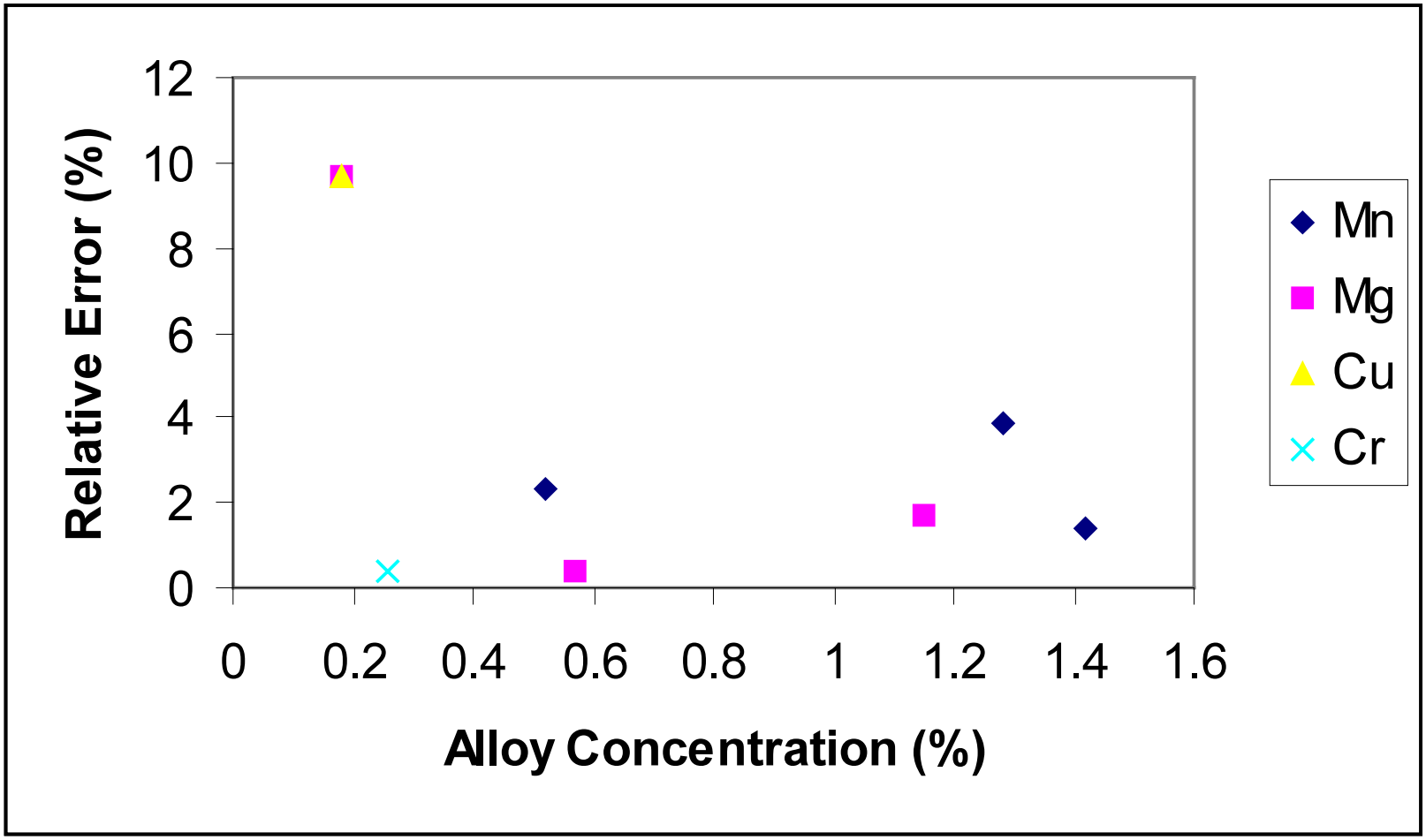
5052 Alloy
Average of 5 Data Sets

	Cr	Mg	Al
Reported	**0.26%**	**0.18%**	**98.54%**
LIBS Meas.	**0.258%**	**0.165%**	**98.51%**
Error	**0.39%**	**9.7%**	**0.03%**

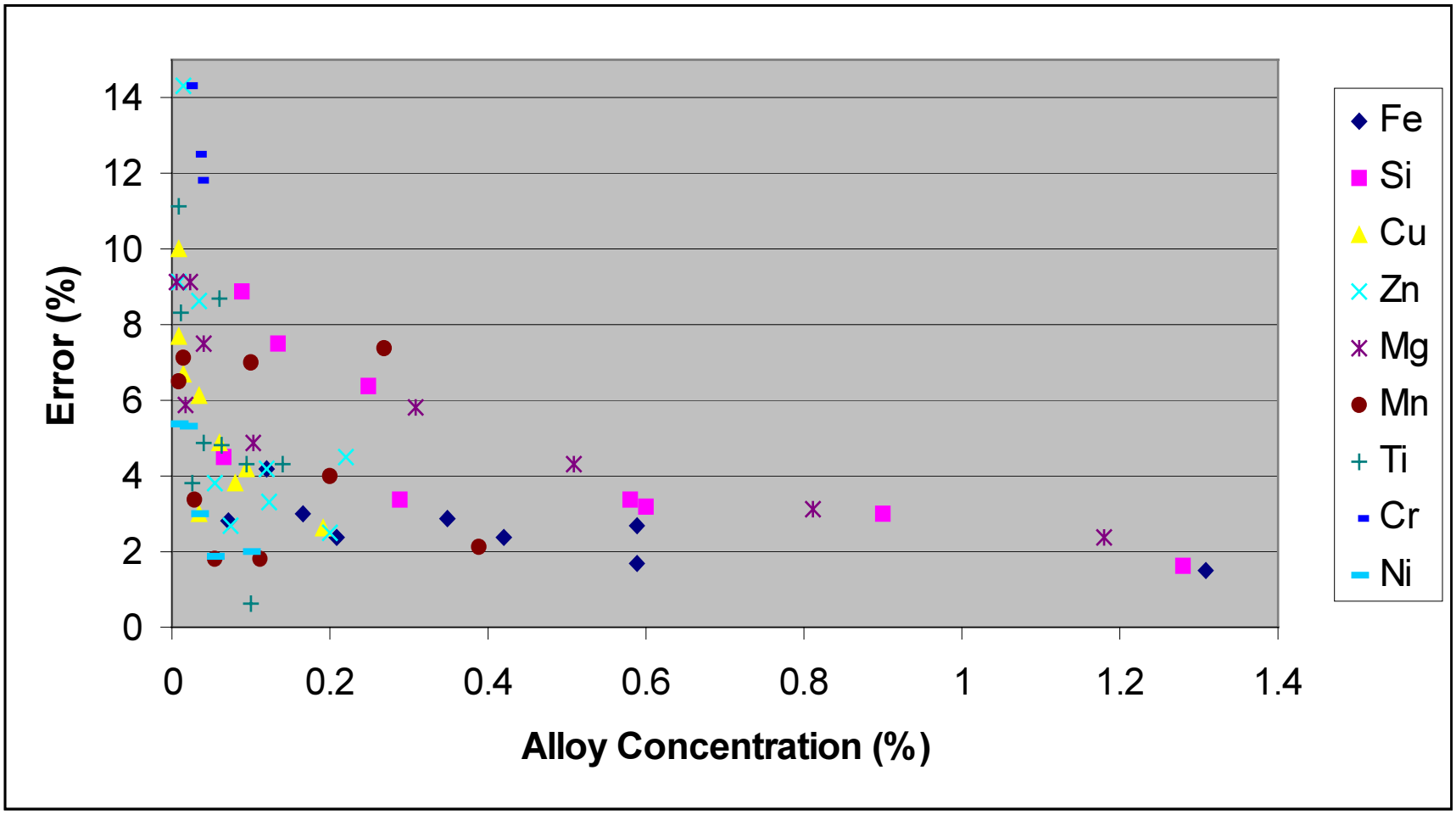
3004 Alloy
Average of 3 Data Sets

	Mg	Mn	Al
Reported	**1.15%**	**1.42%**	**97.34%**
LIBS Meas.	**1.13%**	**1.44%**	**97.31%**
Error	**1.7%**	**1.4%**	**0.027%**

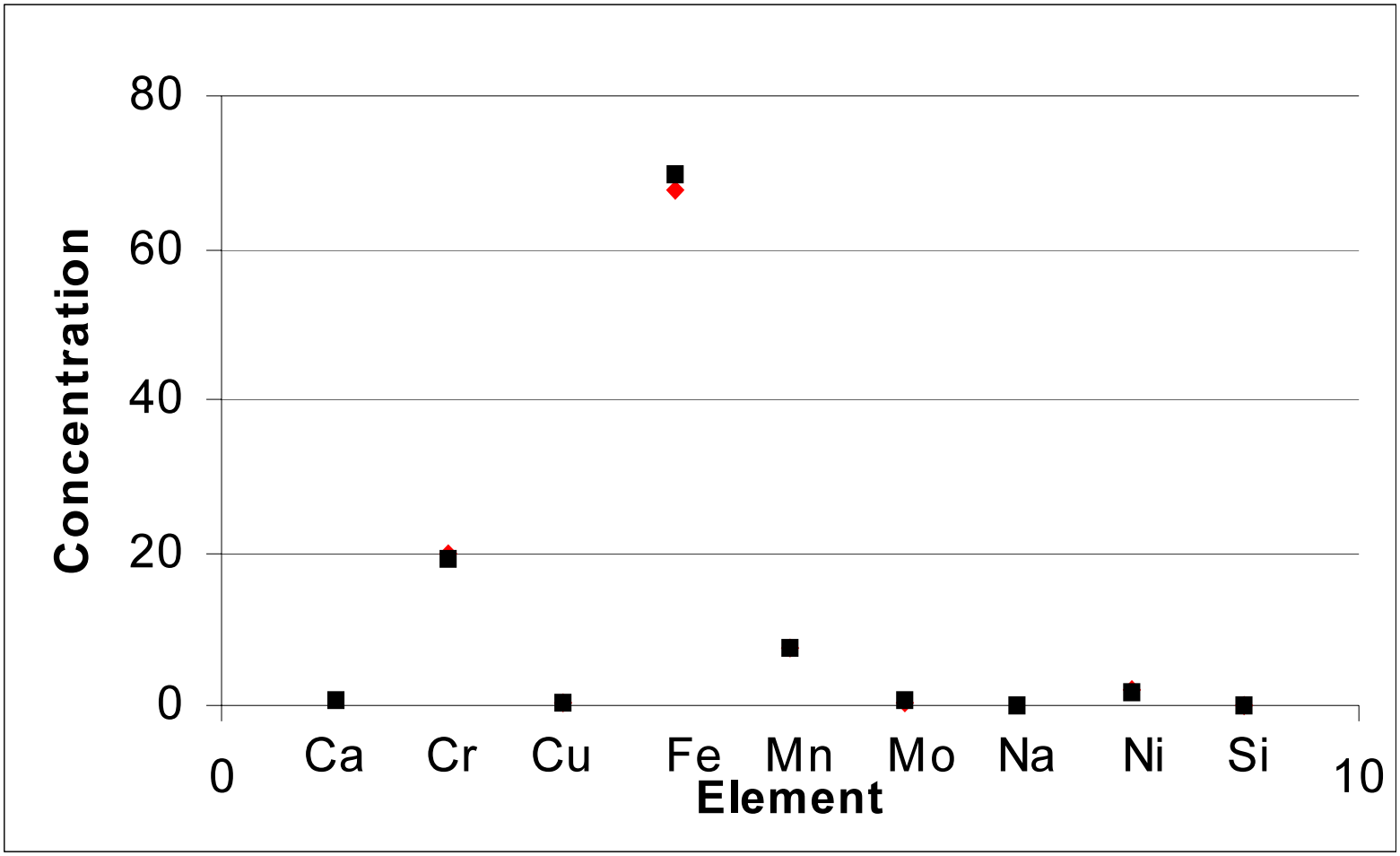
LIBS Measurement Error



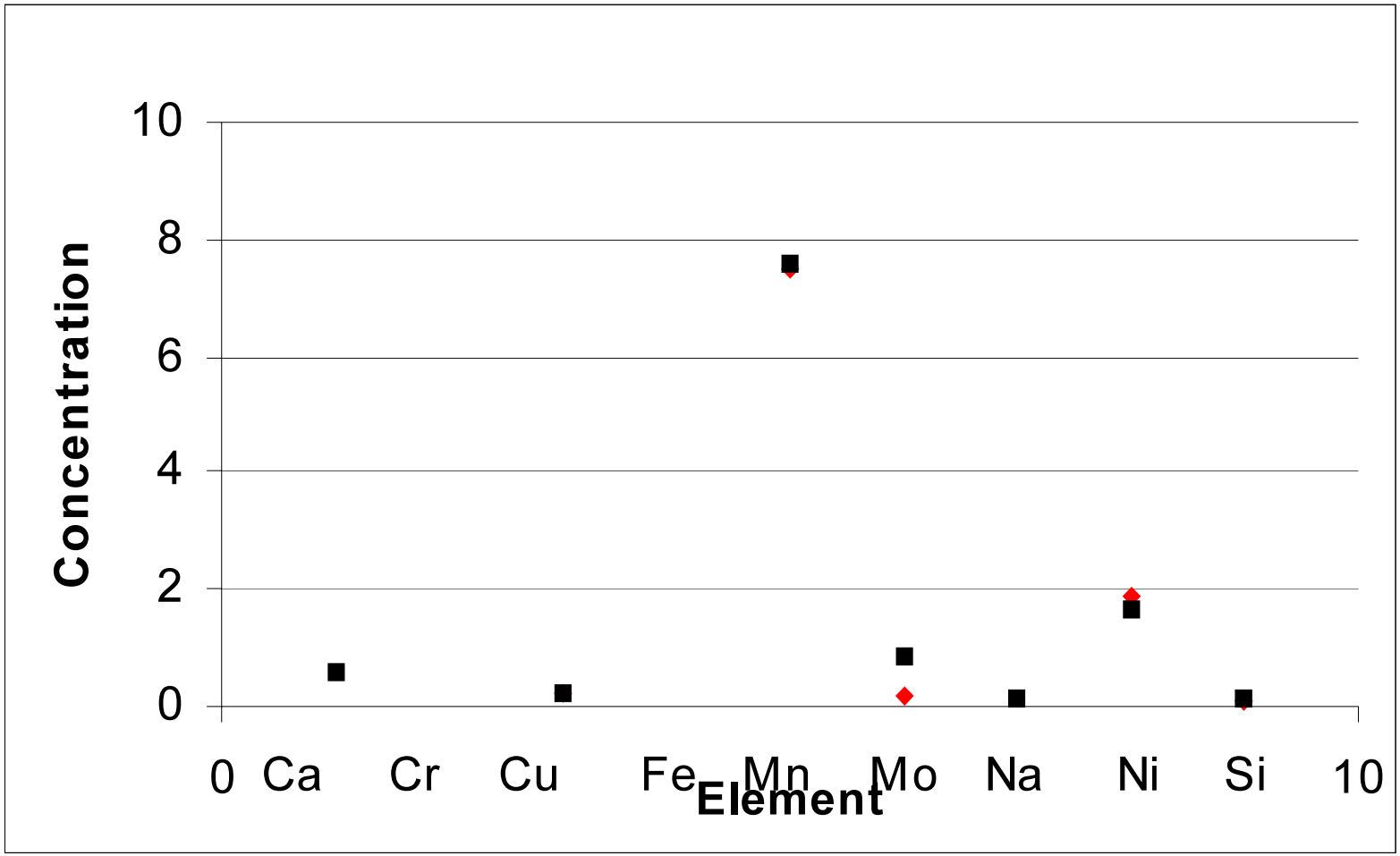
Aluminum Calibration Standards – Reported Errors



Steel Measurements



Steel



Molten Glass Data

Element	Range Of Values Reported		Measured by LIBS	Result	% Outside Range
Si	62.96	61.51	61.01	Good	0.81
Na	29.67	20.72	24.9	Good	
Ca	5.36	3.46	4.8	Good	
Mg	2.71	2.42	2.85	Out	5.2
Ba	4.66	0.00	4.79	Out	2.8
Fe	0.04	0.020	0.02	Good	
Sr	0.04	0.00	0.03	Good	
Mn	0.1	0.00	0.08	Good	

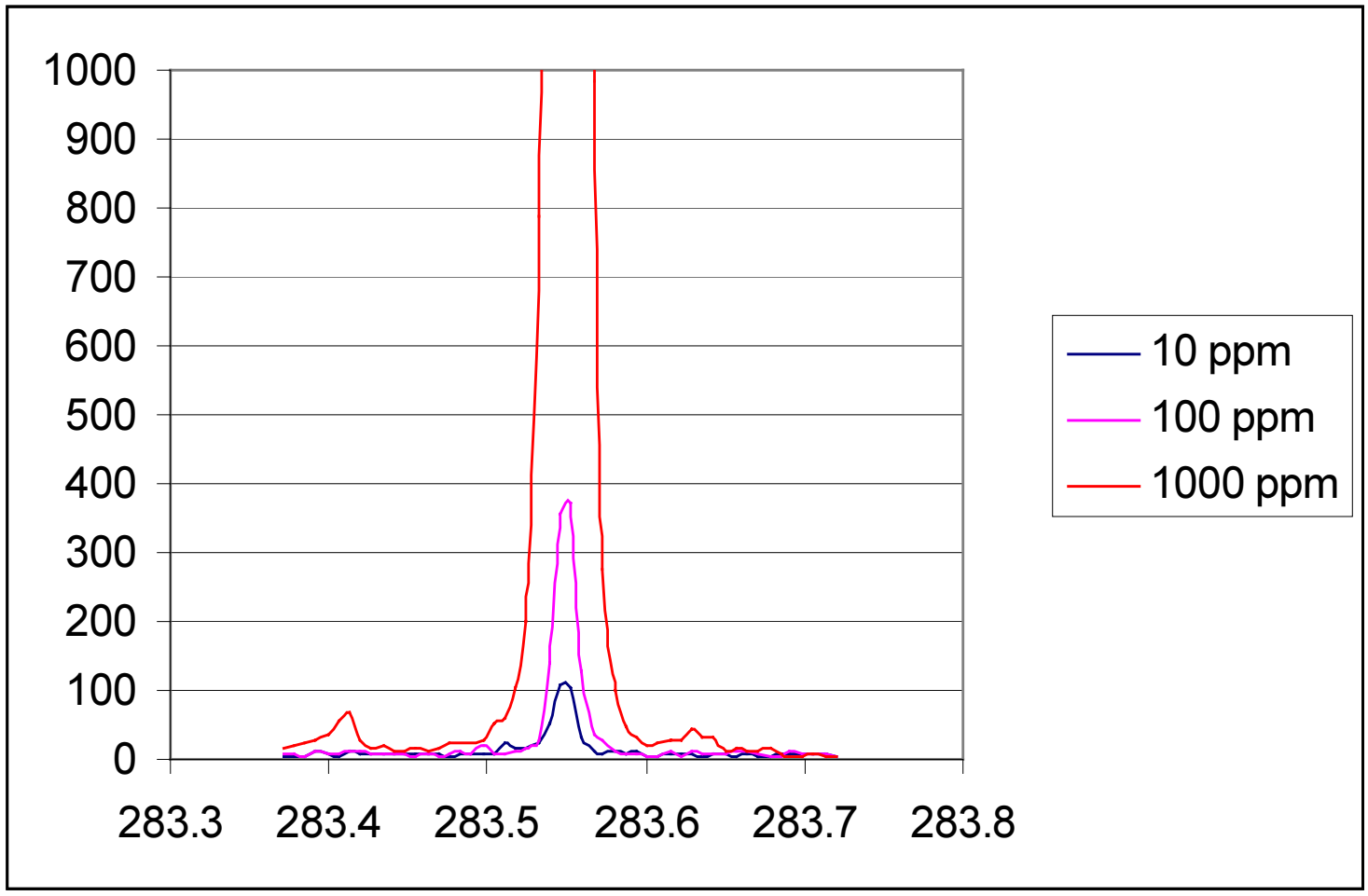
Clay Sample

Element	Computed Concentration (%)	Actual Concentration (%)	Error (%)
Aluminum	50	48	5.0
Iron	0.84	0.91	7.7
Silicon	46.4	49	5.3
Titanium	2.35	2.1	11.9

CF-LIBS Measurement of Various Materials

	Basalt	Limestone	Hematite
SiO_2	17.93%	0.02%	1.74%
Al_2O_3	9.65%	0.27%	3.52%
Na_2O	0.92%		
MgO	48.01%	3.03%	0.11%
$CaCO_3$	15.28%	96.7%	0.10%
Fe_2O_3	7.39%	0.01%	94.45%
TiO_3	0.8%	0.01%	0.09%

Cr Limits of Detection



Measured Limits of Detection (S/N=3)

Element	LIBS Measured Limit (ppm)
Cr	4
Fe	10
Mn	3
Mg	1.4
Cu	60

Limits of Detection by Wein

Element	LOD (ppm)
Li	3
Be	5
Cr	50
Ni	100
Cu	50
Zn	100
Ga	100

Element	LOD (ppm)
Sr	2
Ag	5
Cd	100
Sn	50
Cs	20
Ba	5
Pb	50

Constraints on Accuracy

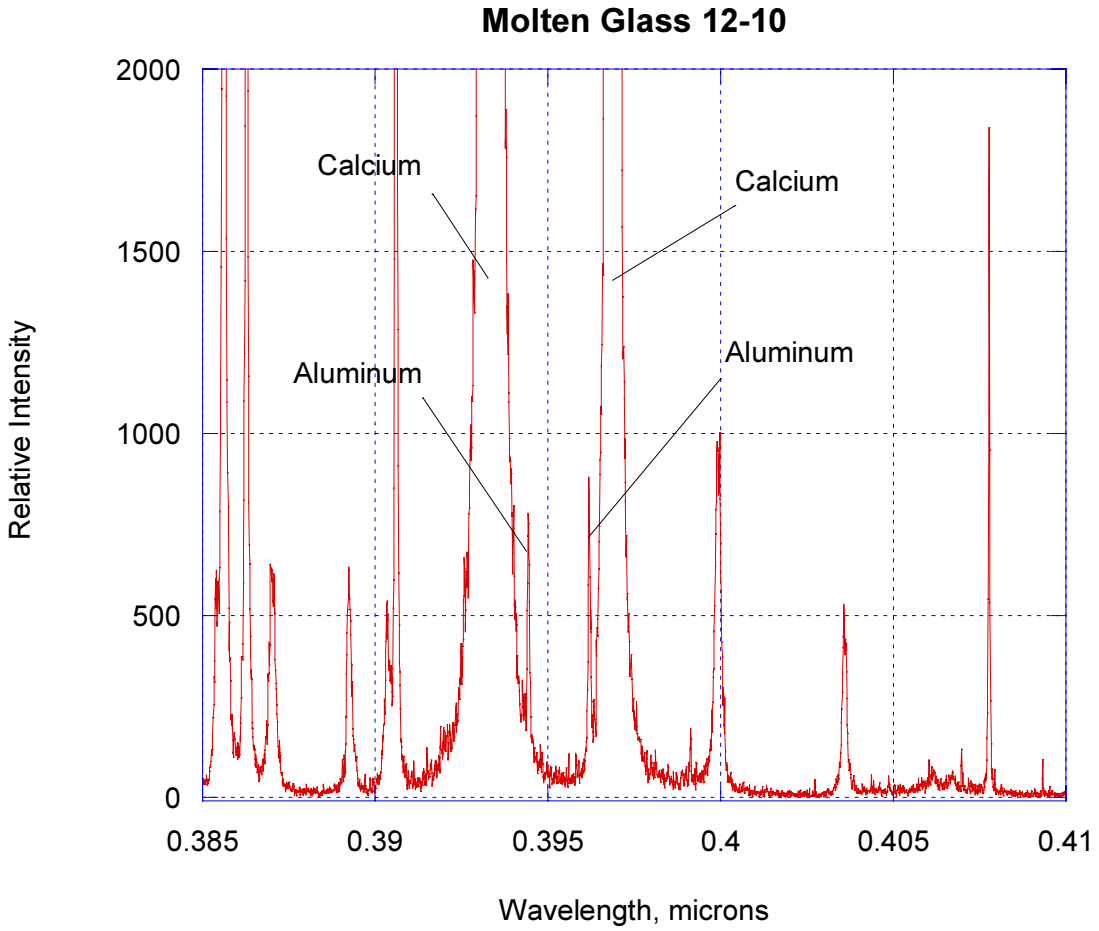
- **Signal to Noise**

Metal	Sample 1 Mean Error (%)	Sample 2 Mean Error (%)	Signal/Noise
Al	2.0	1.9	Good
Si	1.8	2.3	Good
Ti	2.8	6.9	Good
Fe	8.5	13.5	Poor

Constraints on Accuracy

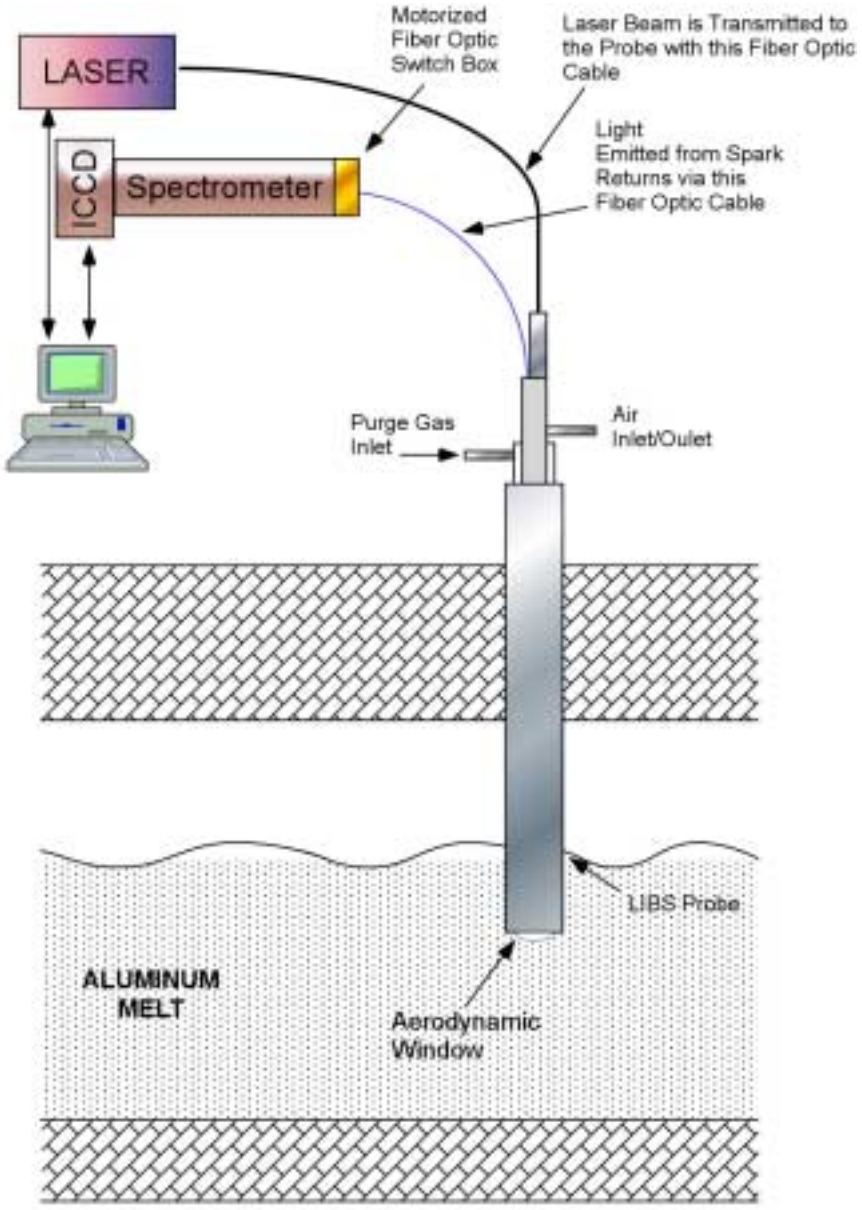
- **Signal to Noise**
- **Overlapping Peaks**

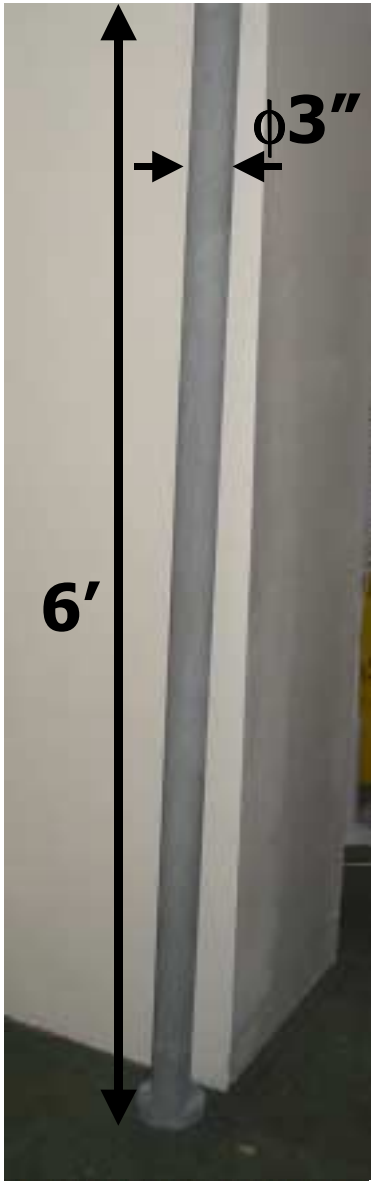
Overlapping Peaks

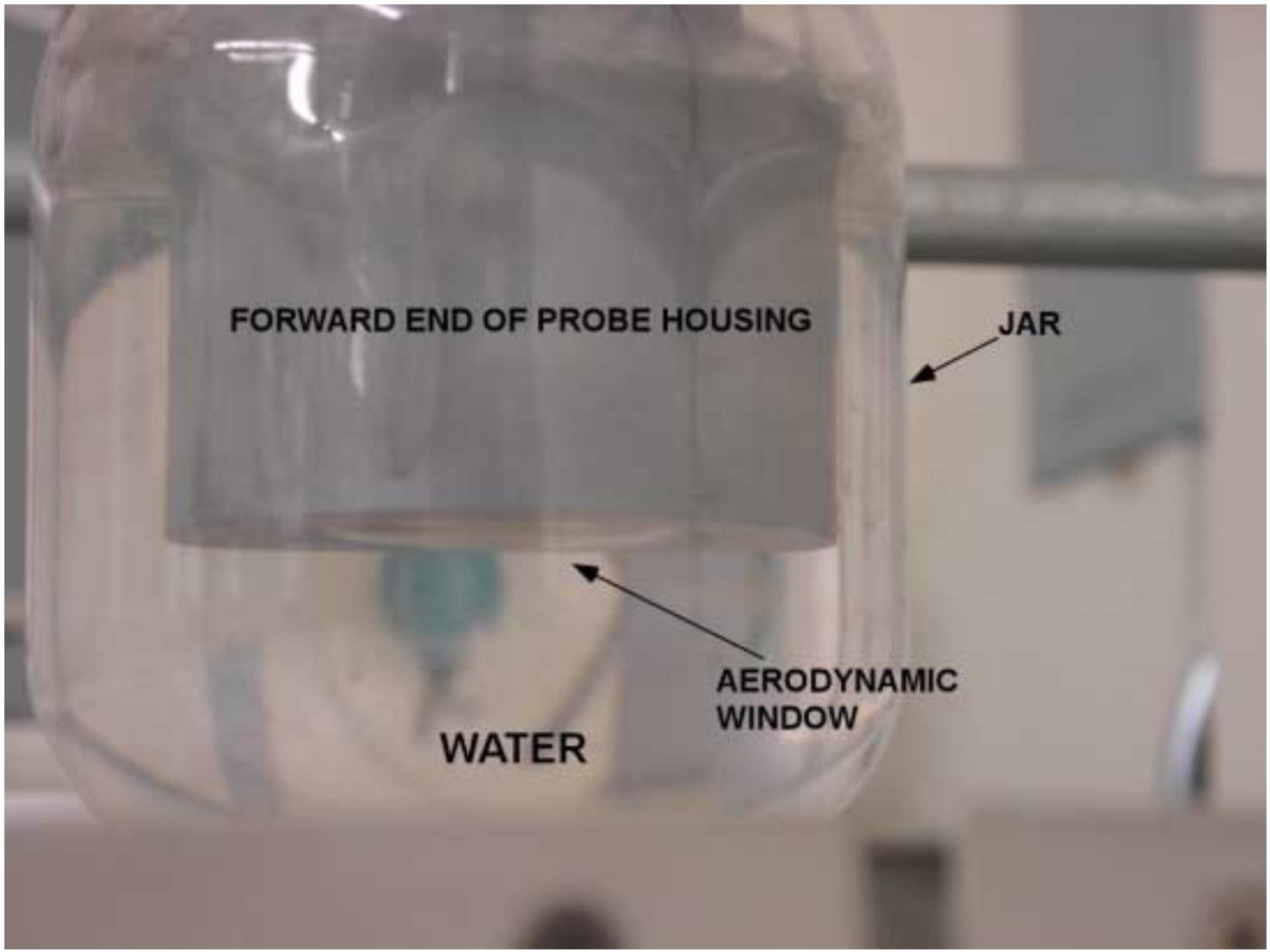


Constraints on Accuracy

- **Signal to Noise**
- **Overlapping Peaks**
- **Self Absorbed Lines**
- **Inaccurate Elemental Physical Constants**
- **Template Departure**


LASER
Motorized
Fiber Optic
Switch Box
Laser Beam is Transmitted to
the Probe with this Fiber Optic
Cable
ICCD
Spectrometer
Light
Emitted from Spark
Returns via this
Fiber Optic Cable
Purge Gas
Inlet
Air
Inlet/Oulet
LIBS Probe
ALUMINUM
MELT
Aerodynamic
Window


ϕ3″
6′


FORWARD END OF PROBE HOUSING
JAR
AERODYNAMIC
WINDOW
WATER

Probe Material

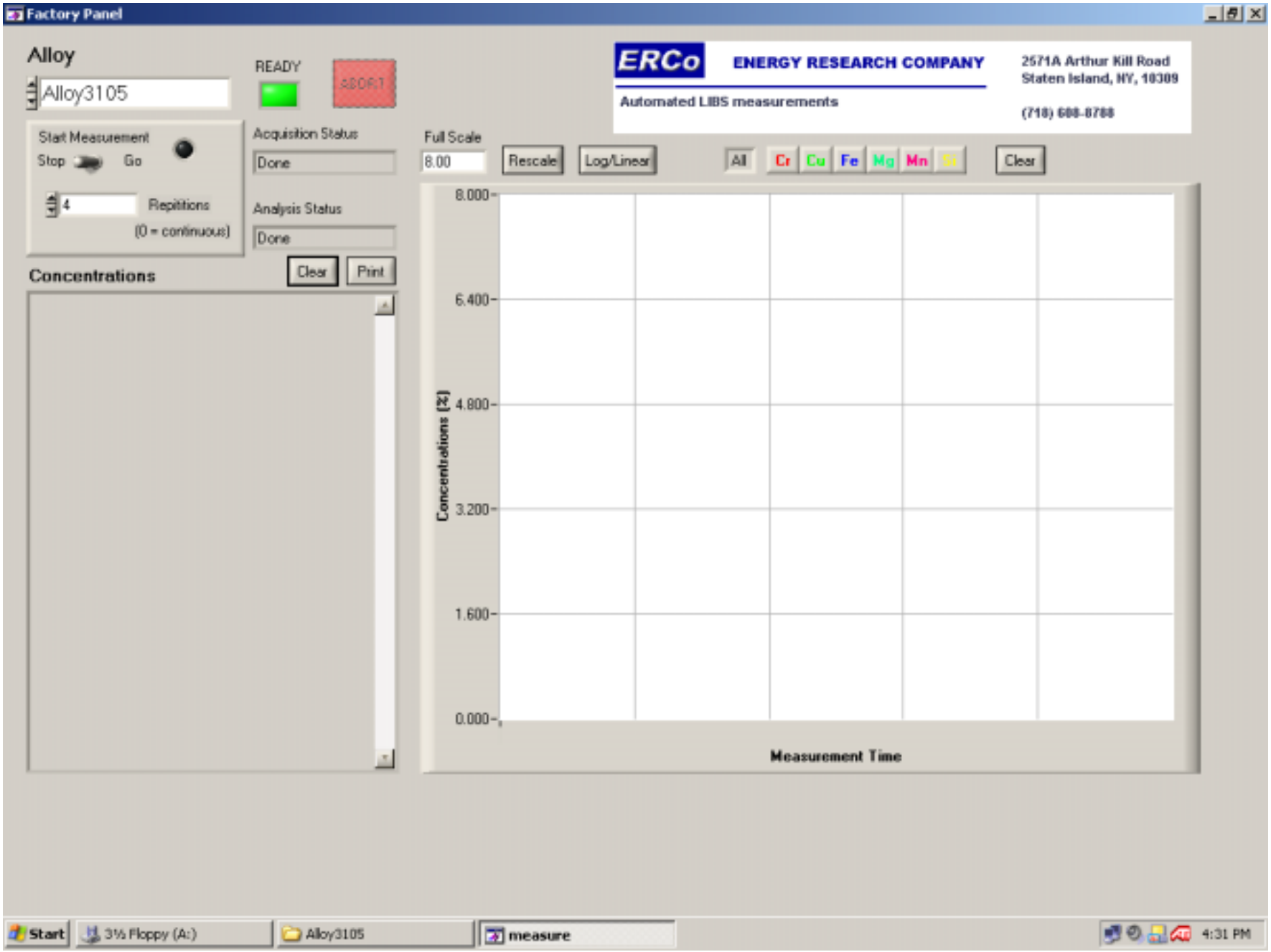
- **SiC Alumina Bonded**
- **Maximum Service Temperature of 1500 ^{o}C**

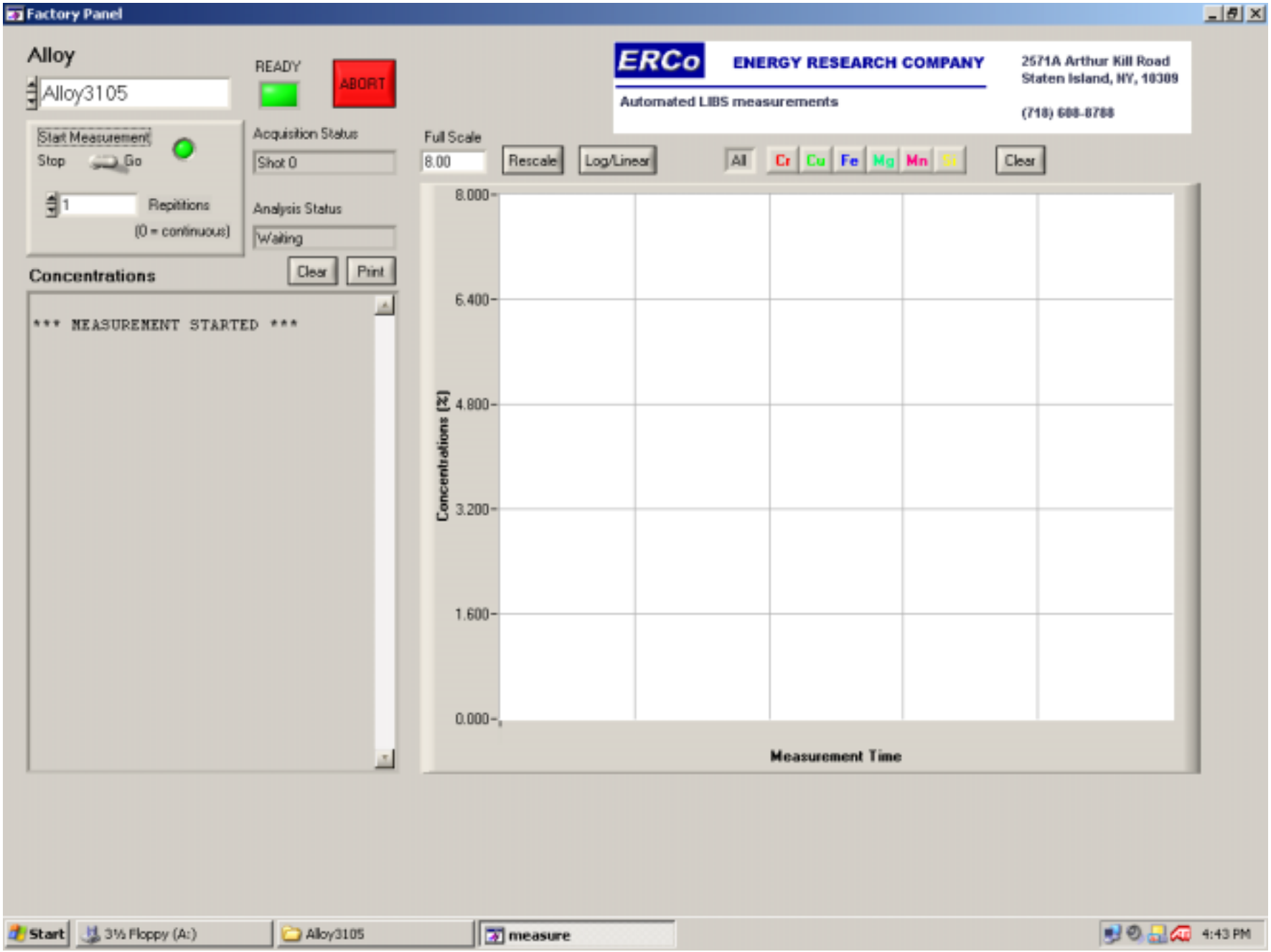
Probe Longevity

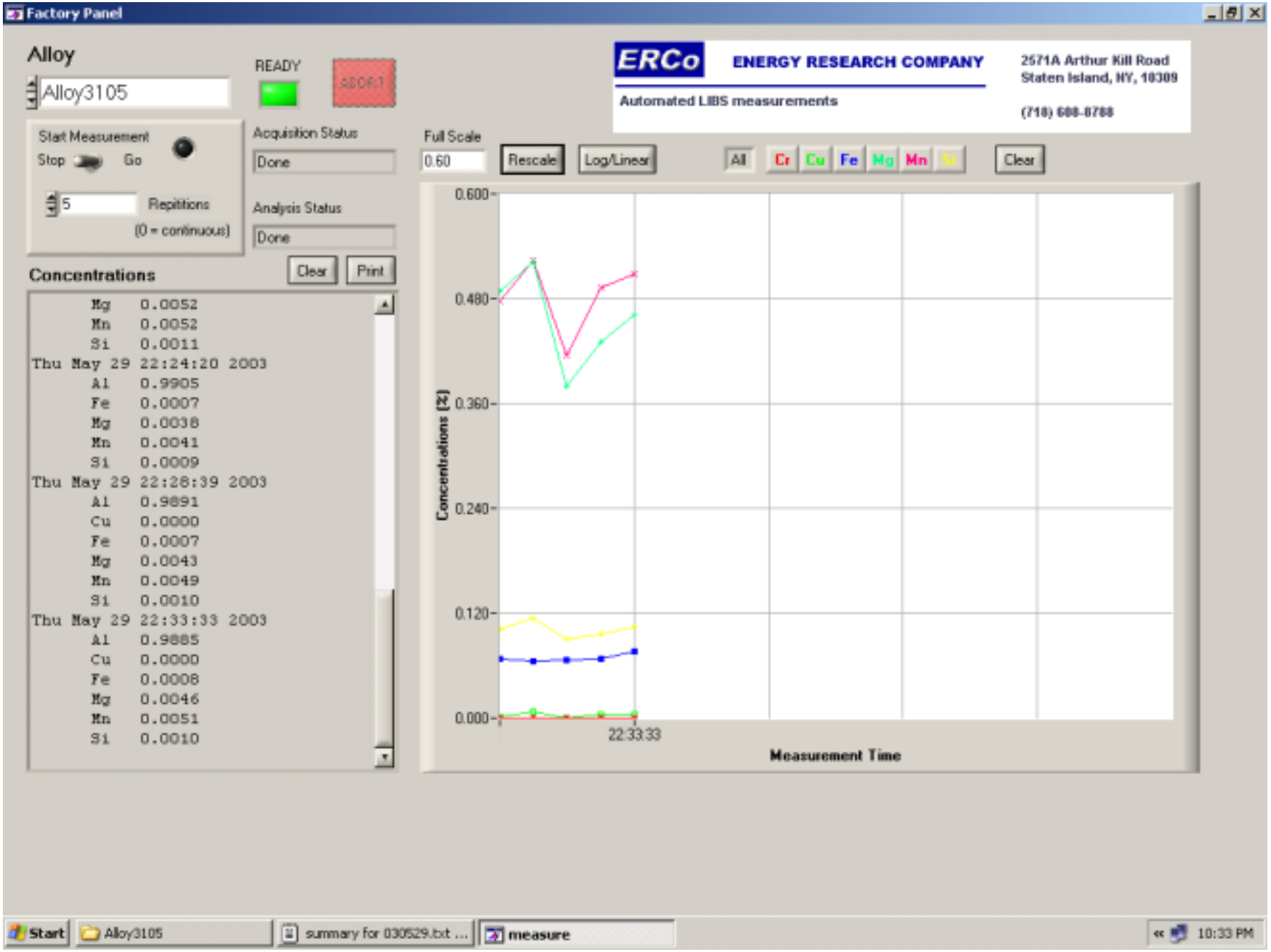
- **Material Compatibility Test – 1426 Hours in Melt without Weight Change**
- **134 Hours in Melt with No Damage**

Maintenance

- **Change Water for Laser and Spectrometer 3 to 6 months**
- **Replace Flash Lamp Every Two Years or So – Requires Service Call**
- **Service Call Every 6 to 12 Months**
- **Probe Replacement**


Factory Panel
Alloy
Alloy3105
READY
ABORT
ERCo
ENERGY RESEARCH COMPANY
2571A Arthur Kill Road
Staten Island, NY, 10309
Automated LIBS measurements
(718) 608-8788
Start Measurement
Stop
Go
4
Repitions
(0 = continuous)
Acquisition Status
Done
Analysis Status
Done
Full Scale
8.00
Rescale
Log/Linear
All
Cr
Cu
Fe
Mg
Mn
Si
Clear
Concentrations
Clear
Print
8.000
6.400
4.800
3.200
1.600
0.000
Concentrations [%]
Measurement Time
Start
3½ Floppy (A:)
Alloy3105
measure
4:31 PM


Factory Panel
Alloy
Alloy3105
READY
ABORT
ERCo
ENERGY RESEARCH COMPANY
Automated LIBS measurements
2571A Arthur Kill Road
Staten Island, NY, 10309
(718) 608-8788
Start Measurement
Stop
Go
1
Repitions
(0 = continuous)
Acquisition Status
Shot 0
Analysis Status
Waiting
Full Scale
8.00
Rescale
Log/Linear
All
Cr
Cu
Fe
Mg
Mn
Si
Clear
Concentrations
Clear
Print
*** MEASUREMENT STARTED ***
8.000
6.400
4.800
3.200
1.600
0.000
Concentrations [%]
Measurement Time
Start
3½ Floppy (A:)
Alloy3105
measure
4:43 PM


Factory Panel
Alloy
Alloy3105
READY
ABORT
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ENERGY RESEARCH COMPANY
Automated LIBS measurements
2571A Arthur Kill Road
Staten Island, NY, 10309
(718) 608-8788
Start Measurement
Stop
Go
5
Repititions
(0 = continuous)
Acquisition Status
Done
Analysis Status
Done
Full Scale
0.60
Rescale
Log/Linear
All
Cr
Cu
Fe
Mg
Mn
Si
Clear
Concentrations
Clear
Print
Mg 0.0052
Mn 0.0052
Si 0.0011
Thu May 29 22:24:20 2003
Al 0.9905
Fe 0.0007
Mg 0.0038
Mn 0.0041
Si 0.0009
Thu May 29 22:28:39 2003
Al 0.9891
Cu 0.0000
Fe 0.0007
Mg 0.0043
Mn 0.0049
Si 0.0010
Thu May 29 22:33:33 2003
Al 0.9885
Cu 0.0000
Fe 0.0008
Mg 0.0046
Mn 0.0051
Si 0.0010
0.600
0.480
0.360
0.240
0.120
0.000
Concentrations [%]
22:33:33
Measurement Time
Start
Alloy3105
summary for 030529.txt ...
measure
10:33 PM

Why Concept is Feasible Now

- **ERCo has Developed a Probe for Molten Aluminum**
- **ERCo has Developed Calibration Free Measurements**
- **Rugged Broadband Spectrometers Are Now Available**
- **Rugged Lasers Are Now Available**
- **Funding from DOE**

Technical Progress and Outlook

Demonstration at Commonwealth

Industrial End-User Involvement

- **Aluminum**
  - Commonwealth
  - Century
  - Logan
- **Glass**
  - PPG
  - Fenton
  - Kopp
  - CertainTeed
- **Steel**
  - Crucible
- **Coal**
  - CQ Inc.
  - Ontario Power
  - Colorado Springs Utility
  - Southern Company

Market Potential

- **Commercialization Plan Completed**
- **Licensee Agreement Signed**
- **Patents Pending in US, EU, Canada, and soon Japan**
- **First Overseas Sale Completed**

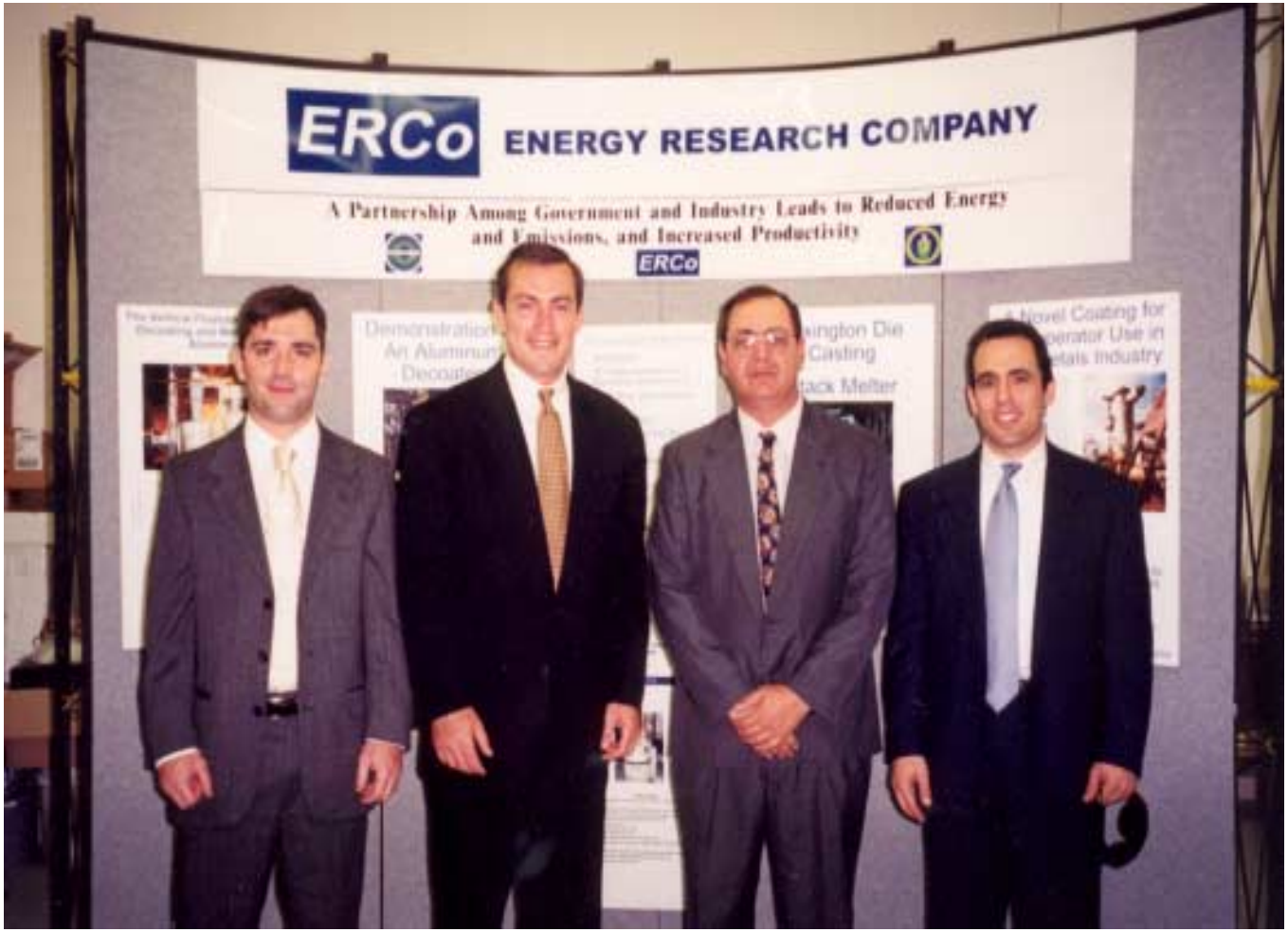
What's Next

- **Demonstration at Commonwealth (Aluminum)**
- **Demonstration at Crucible (Steel)**
- **Demonstration at PPG (Glass)**
- **Sales to Al Industry Through Licensee**
- **Development for Coal**

Energy Savings

	Energy Savings by 2010 (Trillion Btu)
Molten Glass	**4.2**
Molten Aluminum	**9.2**
Total	**13.4**

Congressman Fossella (R-NY)



Summary

- **LIBS System Proven in Lab**
- **Calibrationless Technique Development Completed**
- **Software and Design Allows Single Pushbutton Operation**
- **Minimal Operator Training Required**
- **Maintenance Simple**
- **Patents Pending**
- **Demonstration at Commonwealth to Start in June**
- **First Commercial Sale Made**